Thermal Analysis Study of the High Temperature Phase Transition in KH_2PO_4

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According to the phenomenological model proposed by Imry *et. al* [1], potassium dihydrogen phosphate (KH_2PO_4) has two correlated phase transitions at temperatures T_1 and T_2. The low temperature phase transition was associated with the Curie point (T_1 = -150°C) [1].. The nature of the high temperature phase transition was not, however, specified. .There have been a number of publications that report anomalies in various physical properties in the vicinity of 180°C. . These anomalies have been repeatedly explained as resulting form a polymorphic (tetragonal to monoclinic) phase transition.. The temperature ~180°C is often considered as the temperature of the polymorphic transition, T_2. .Recently, Lee [2] demonstrated that various anomalies in physical properties observed around 180°C can be alternatively explained as a result of dehydration of KH_2PO_4 and formation of a polymeric residue $(KPO_3)_n$. . This opinion is also supported by Ortiz *et. al* [3].

The present study employs the method of thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) to examine the thermal properties of KH_2PO_4 on heating up to the melting point (~250 °C). TMA demonstrates that both loose powder and pressed pellet have an anomalous thermal expansion in the temperature region 200 – 220°C. The anomaly is explained by the occurrence of a sluggish polymorphic transition. Heating of KH_2PO_4 in a DSC apparatus does not allow one to detect the thermal effect associated with the polymorphic phase transition because of substantial endothermic dehydration. However, the effect is observed on cooling of samples preheated to the temperatures of 215 - 235 °C. Although the samples cooled after the transition remain in the high temperature metastable form, the transition is found to be reversible. The reverse transition is very slow and may take up to 24 hours to occur at 120 °C.

[1] Y. Imry, I. Pelah, and E. Wiener, *J. Chem. Phys.* **11**, 2332 (1965).
[2] K.-S. Lee, *J. Phys. Chem. Solids* **57**, 333 (1996).
[3] E. Ortiz, A. Vargas, and B.-E. Mellander, *J. Phys. Chem. Solids* **59**, 305 (1998).